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German Patent Application DE 198 02 791 A1

Title: Method for Producing Aerosols, Powders and Layers of Glass and Ceramics by Means of Electroflame Spraying

For: PPG Industries, Inc. – Intellectual Property – Glass Dept.

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(19) Federal Republic of Germany

German Patent and Trademark Office

(12) **Unexamined Patent Application**

(10) **DE 198 02 791 A1**

(21) File No.: 198 02 791.5
(22) Filing Date: January 26, 1998
(43) Disclosure Date: July 29, 1999

(51) Int. Cl.[6]:
B 01 J 19/08
B 01 D 1/14
C 04 B 35/622
C 04 B 41/85
C 03 C 17/04
C 03 C 17/23
C 23 C 4/12
C 09 K 3/30
C 09 D 5/46
B 05 B 5/00
B 05 B 7/20

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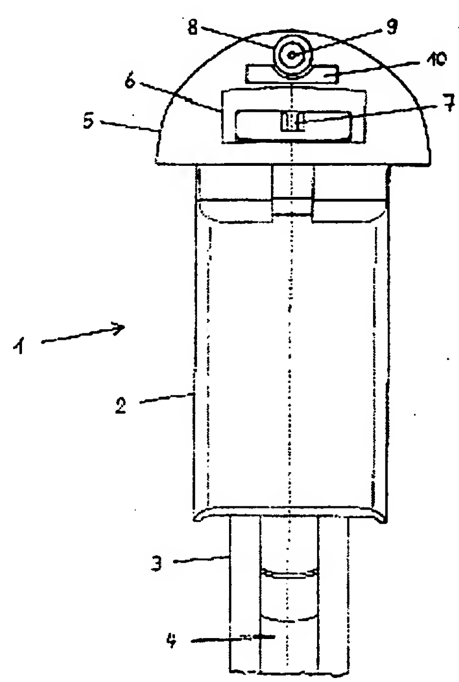
The following text is taken from documents filed by the applicant

(54) **[Title of the Invention]:** **Method for Producing Aerosols, Powders and Layers of Glass and Ceramics by Means of Electroflame Spraying**

(57) **[Abstract]** This invention relates to a method for producing aerosols, powders and layers[1] of glass and ceramics by electrospraying, in which a liquid which may be a melt or a suspension or a reactive liquid, is sprayed directly into a flame by means of electrospraying. No auxiliary electrode is used in this case and instead the flame itself serves as the counter-electrode so that the particles cannot lose their charge as the pass through an auxiliary electrode. As a result of the method according to this invention, nano-scale powders can also be produced and layers can be produced from them.



[1] **Translator's Note**: the German term "Schicht" foremost has the general meaning of "layer", the term used in this translation. It can, however, also mean "coat," "coating" or "film."

Description

The invention relates to a method for producing aerosols, powders and layers of glass and ceramics. Such layers are referred to as a layer of glaze, enamel or ceramic for improving or modifying the optical, mechanical, thermal and chemical properties of the materials. This invention relates in particular to the production of very small nano-scale particles, so the process temperature for forming a dense layer can be reduced greatly because of the increased sintering activity. This method is therefore recommended in cases when the substrate can be exposed only to lower temperature treatments.

Chemical processes such as sol-gel processes, gas-phase deposition or precipitation from liquids are usually used to produce nano-scale particles. However, these processes are associated with various disadvantages such as the high cost of the starting materials, low rates of deposition and the formation of solid aggregates from the particles thus generated. The mechanical methods such as milling, crushing and stress-crushing constitute a large group of physical methods. However, these methods are not suitable for an economical production of powders having particle diameters in the nm range; furthermore, powders produced with the help of these methods have poor flow properties because instead of spherical particles, these methods usually yield splintery particles. Another group, which can also be included with the physical powder production methods, includes the spray processes, e.g., spray drying, atomization and electrospraying of liquids. When applied to a substrate, the powders produced in this way can be compressed by thermal processes to form a dense layer or they can be deposited directly as a layer by means of thermal spray processes (e.g., flame spraying, plasma spraying).

In the production of nano-scale glass and ceramic powders, flame hydrolysis has proven to be advantageous in comparison with other chemical synthesis methods. In the case of flame hydrolysis, mainly the high production rate, the relatively inexpensive starting materials, the low equipment complexity and the fact that they can be produced in just one production step [1, 2] should be mentioned. This process is usually carried out with the help of a countercurrent method for the combustion gases [3]. Tikkanen et al. [4, 5] presented the so-called LFS method (Liquid Flame Spray) which is a combination of flame synthesis and flame spraying. In this case, a precursor liquid is drawn out of a capillary through the gas stream passing by the capillary as a result of which it is atomized. The droplets of liquid with sizes of a few µm to

60 μm react in the flame to form the product. The size of the droplets depends on the surface tension and viscosity of the liquid as well as the gas flow rate. For aqueous solutions, larger particles have been observed than for organic solutions and the droplet size decreased with an increase in gas flow rate. The flow rate was 5 mL/min. The particles were deposited electrostatically with a deposition rate between 5 and 20 mg/min. In contrast with traditional flame spray methods in which powders or suspensions are used and therefore with said powders first having to be produced in processes which are sometimes complex, the powder particles, in the case of the LFS method, are formed directly from the precursor liquid as a result of chemical combustion reactions. This method becomes problematical when droplets of liquid having a smaller diameter are required, because there is a limit due to the spray pressure and the nozzle opening.

Therefore, production of aerosols by means of electrospraying is recommended because aerosols with droplet diameter in the nm range can also be produced when suitable liquid properties exist. In the case of the electrospray process, an electric field is generated between a point-plate arrangement, where the point is a liquid droplet. Due to the high electric field, the droplet is deformed to a cone, the so-called Taylor cone, with a stream opening out of the tip of the cone. The stream is divided into fine droplets as a result of Rayleigh instabilities, which are based on the repulsive forces of the electric charges in the stream. A detailed description of the electrospray process and the parameters can be found in [6] by Michelson. Chen et al. [7] proposed a temperature treatment of the resulting aerosols. They introduced aerosols produced by means of electrospraying into a flame. The statement of the problem on which their work is based consists of the introduction of the stream (consisting of heptane droplets) into the flame. In the opinion of the authors, it is impossible to spray the aerosol directly into the flame because first of all, the environment of the flame has a punch-through voltage[1] that is too low due to the high concentration of ions and therefore a continuous spray process cannot be established. In the opinion of these authors, the electric field must therefore be shielded from the flame. Secondly, however, the speed of the aerosol is also too high (a droplet speed of 10 m/s is stated in this case) so the droplets fly through the flame without being affected by it. As a remedy, an electrode system consisting of two parallel wire mesh pieces having the same polarity is used. The electrode closer to the capillary is used to produce the aerosol and the neutral-field space

[1] **Translator's Note**: other possible translations are "breakdown voltage" or "puncture voltage."

between the two electrodes is used for decelerating the droplets. In addition, a few droplets are dispersed by the impact on the mesh pieces, forming a mixture of larger droplets and a fine mist. However, this has the result that a monodispersed aerosol is no longer present. The flame originates form above the second mesh. As another possibility, Chen et al. [8] proposed producing an aerosol with the conventional point-plate configuration, where the stream of liquid droplets is ignited after crossing the wire mesh, which is wired as the counter-electrode. The shape and intensity of the flame can be controlled by means of varying a stream of gas feed in coaxially. One disadvantage of the methods described above is that the particles must first pass an auxiliary electrode that is wired as a counter-electrode, which may thus have a negative effect on their charge and speed of flight through the air.

The electric field has an influence on the shape of the flame and its temperature. Studies of the influence of a radial electric field on the flame temperature and flame shape for propane-butane flames have been reported by M. Zake in [9] and [10]. A positively polarized wire electrode is placed at the center of a burner, resulting in the transport of electrons into the center of the flame and a movement of the positive ions in the opposite direction and causing the creation of a shield made of positive ions at the edge of the flame. As a result of introducing air into the flame, these authors observed an increased combustion reaction at the center of the flame with a resulting increase in temperature. The maximum flame temperature was measured when the amount of air added was stoichiometric for combustion of the gas. As a result of increasing the gas flow rate, a higher gas velocity was achieved, so that the radial convection of the gas particles due decreased as a result of the electric field.

In addition, according to Nguyen and Chung [11], it is possible that because of the electric field, droplets of liquid may become elongated in a flame in which a central electric field prevails and may thereby be dispersed into smaller droplets.

Various conventional methods have been used for producing layers; first, multistep processes can be mentioned in which a powder layer is applied to a substrate first and then in a second step is sintered-on and/or melted-on with the help of a secondary thermal treatment in order to form a dense layer. A layer can be applied with the help of a wide variety of techniques such as pressure spraying, vapor deposition, etc. In addition, there are also one-step processes such as electrospraying of metal melts and/or of glass melts, a process which has previously been performed only on a laboratory scale [12], in which case molten droplets are sprayed directly

onto a substrate, where they form a dense layer. However, this process can be carried out only in vacuo and it has very low rates of deposition. In addition, thermal spray methods (e.g., flame spraying, plasma spraying) can also be mentioned in this context where a free-flowing powder is introduced into a flame, melted in the flame and then sprayed onto a substrate at a high speed. These methods have the disadvantage that they require the use of powders having particle diameters larger than 10 μm in order to achieve a sufficient free-flowing property. Accordingly, the melted-on powder particles are also very large. Although these particles may be dispersed into smaller particles on striking the substrate, the resulting layer is usually porous due to the high cooling rate. An improvement is possible with the help of vacuum spray methods, but this significantly increases the cost of coating because of the higher investment costs and costs of operations.

The task of this invention is to design a method and a device as described in the preamble, so that an aerosol consisting of electrically charged liquid droplets with a size distribution in the nm to μm range is sprayed directly into a flame, and the particles generated as a result, depending on the application, are processed further as an aerosol or filtered out as a powder or sintered onto a substrate directly in situ as a dense layer,.

This task is solved by the method according to the invention, which represents an advantageous combination of the conventional methods of flame spraying and electrospraying. In the case of the method according to the invention, a liquid which may be a melt or a suspension or a reactive liquid is sprayed directly into a flame by means of electroflame spraying. In this case, no auxiliary electrode is used, but instead the flame serves as the counter-electrode, so that particles cannot lose their charge in their passage through an auxiliary electrode. This method surprisingly permits direct spraying of the droplets emitted from the Taylor cone, contrary to the data found in the literature [7]. The high electric field strength required for the generation of the Taylor cone does not differ significantly from that of a spray-plate arrangement having equal electrode spacings. It depends on the properties of the liquid and the equipment furnished and is usually in the range between 1 kV/cm and 30 kV/cm. The resulting aerosol may then be deposited on a substrate for the purpose of the formation of a layer or it may be filtered out of the aerosol stream as a powder with the help of suitable devices or it may be processed further directly as an aerosol. This method constitutes an atmospheric spray

method which also permits the production of dense glass and ceramic layers by means of directly sinter-fusing the deposited particles.

This invention constitutes a combination of electrospraying with flame spraying and combines the advantages of both methods. The electrospray process allows the production of extremely fined electrically charged droplets from a liquid. In contrast with conventional electrospray processes, the flame serves as the counter-electrode and no auxiliary electrode is used, which ensures that the droplets cannot lose their charge in their passage through an electrode before entering the flame. The electrically charged droplets that enter the flame react to form the product as they do in flame spray processes. In addition, effects can also be observed due to the electric charge of the droplets in the flame. Under favorable conditions, the droplets are dispersed in the flame because of their high electric surface charge by developing an ellipsoidal shape due to the prevailing electric field and dispersing further due to Rayleigh instabilities. In the case of a suspension as the starting liquid, this results in the powder particles thus obtained, which are formed due to solidification of the liquid droplets, having a smaller size than the primary particles of the starting powder. In addition, the size of the particles is influenced by the spray angle. As a result of using suitable [vapor-]deposition equipment, a powder that can be processed further can be obtained from the aerosol or a dense layer can be produced directly.

Details regarding the method according to the invention are explained in greater detail below with reference to the drawings:

Figure 1 shows a schematic view of a device for electroflame spraying;

Figure 2 shows a detail of a schematic view of a device for electroflame spraying;

Figure 3 shows a detail of a schematic view of another device for electroflame spraying with a central introduction of the aerosol into the flame zone.

Figure 1 shows a device consisting of a metal capillary **4** which is attached by an electrically insulating feed line **3** to a liquid reservoir **2**, a suitable burner **12** and a substrate **23**.

By means of a delivery apparatus **1**, which is not described in greater detail here, the liquid is conveyed from a suitable electrically insulated reservoir **2** through the feed line **3** into the capillary. The position of the capillary **4**, which is which is held in place by a mount **8**, may be varied both horizontally and vertically with the help of a suitable displacement and lifting device **7**. In addition, the angle between the capillary **4** and the burner **12** can be varied

continuously by a rotating device **5** connected to the mount **8**. The combustion gases are supplied to the burner **12** from gas reservoir **15** and **16** through feed lines **17** and **18**. The gas pressure is continuously adjustable through suitable valves **13**.

The electric field between the flame **14** and the capillary is generated by the fact that the metallic nozzle **11** of the burner **12** is grounded and the electrically conducting capillary **4** is connected to the high voltage of a high-voltage power supply unit **26** (not described in greater detail here) via a line **9** (not described in greater detail here). Because of the high ion concentration in the flame, it has a sufficient electric conductivity to transmit this electric field.

The deposition of the particles which are have been generated by the flame spraying process is accomplished with the help of a substrate **23**, which will not be identified further here and which is connected by a suitable mounting device **22** to a tilting unit **21** which allows adjustment of any angle between the flame **14** and the substrate **23**. This tilting unit **21** is connected by a suitable mount **20** to a displacement unit **19**, which is not described in greater detail here and which allows a horizontal and vertical displacement of the substrate **23** at a suitable speed.

The further description of this method will be based on **figure 2**, which schematically shows a detail of a device for electroflame spraying. The electric field between the capillary **4** and the flame **14** results in a Taylor cone **24** being formed at the end of the capillary **4** from the liquid conveyed through the feed line **3** out of the reservoir **1**. This Taylor cone **24** opens into a stream which is then dispersed into fine droplets **25** due to Rayleigh instabilities. Because of the prevailing electric field, these droplets **25** mostly enter the flame where they react. If the liquid is a suspension of powder particles in an organic fluid such as ethanol, for example, the fluid will burn up in its approach to the flame and the powder particles present in the original liquid droplets may melt in the flame and become spherical when there is a sufficient supply of heat. In addition, it is also possible for the powder particles to be melted and to experience a further Rayleigh instability due to their residual electric charges and as a result be dispersed further. With the help of this process it is possible to produce particles having a smaller size than the primary particles of the starting powder. In the case of reactive liquids, the droplets in the flame react to yield the corresponding product.

For the production of glass and ceramic layers with the help of the method described in this application, a substrate **23** may be positioned in such a way that the particles are deposited

on the substrate. The particles impinging on the substrate may be sinter-fused there immediately, e.g., by positioning the substrate close enough to the flame. For the production of layers having a uniform thickness, the substrate **23** is moved uniformly with the help of the displacement unit **19**.

If the device presented here is used to produce powders, a suitable substrate must be selected for this purpose. Suitable examples include filter cloths, for example. The diameter of the particles may be varied by the angle α between the capillary **4** and the burner.

Figure 3a shows an embodiment of this invention which permits a more homogeneous distribution of the particles in the flame through central spraying of the liquid droplets into the flame zone. In this process, the nozzles of several burners **12** (**figure 3b** shows eight burners **12** as an example) are arranged in a circle, and the capillary **4** is positioned at the center of this circle. This arrangement prevents some of the powder from flying by the flame so that it does not experience adequate heating.

One embodiment describes the production of an aerosol by electroflame spraying. An aerosol is produced with the help of a device like that illustrated in **figure 1**. A suspension of glass powder, e.g., a ruby red enamel from the Blythe Colours company based on lead oxide, is produced with a high powder content, e.g., 50 wt% of glass powder and an adjusting agent such as polyethyleneimine 10,000 (1 wt%, based on solids content) or hydroxypropyl cellulose in a dispersing liquid, e.g., ethanol. The flow rate of the liquid, which is promoted with the help of a spray pump, is between 5 and 30 mL/min; a flow rate of 8.25 µL/min is regarded as especially suitable for a capillary inside diameter of 2 mm. Hydrogen is used as the combustion gas for low-melting powders, and detonating gas or an acetyle [sic; probably should be: acetylene - translator] oxygen mixture is used for higher-melting powders. A flow rate of 2 slpm (standard liters per minute) is sufficient for hydrogen; higher flow rates are also suitable. The angle α between the capillary and the burner nozzle may be varied between 5° and 50°, e.g., an angle of 20° may be selected; the distance between the burner nozzle and the capillary was varied between 10 and 30 mm. The high voltage on the capillary was between 3 and 8 kV. The resulting aerosol consisted of a gas-powder mixture with powder particles with diameters between 80 nm and 10 µm.

Another practical example describes the production of a powder by means of electroflame spraying. The arrangement of the device and the suspension correspond to the

parameters mentioned in the preceding example. The particles are deposited, for example, electrostatically from the aerosol stream; likewise filtering out through a filter cloth is also possible. The diameter of the spherical powder particles is in a range between 80 nm and 50 μm; given a favorable choice of parameters (such as the possibilities mentioned in the preceding practical example), particle size distributions from 80 nm to 5 μm can be achieved.

The following practical example describes the production of a layer by means of electroflame spraying. The parameters correspond to those in the practical example describing the production of an aerosol by means of electroflame spraying, however, a substrate, specifically a pane of glass in this case, is moved back and forth over the flame at a rate between 1 and 20 mm/s, e.g. at a rate of 10 mm/s. The substrate is aligned perpendicular to the baseline of the burner. Depending on the length and temperature of the flame, the distance between the substrate and the burner nozzle is between 15 and 150 mm, e.g. 40 mm at a gas flow rate of 3.5 slpm of hydrogen and when using the suspension described in the above practical example. The method described above allows the production of sintered glass and/or ceramic layers on the substrate, e.g. production of a colored and transparent enamel layer on a glass substrate. The thickness of the layer may be varied by way of the treatment time per unit of area.

In another practical example, the production of a glass layer on silica glass by means of electroflame spraying is described as a result of the electroflame spraying of a reactive liquid. For production of a sinter-fused silica glass layer on a silica glass substrate, the apparatus described in the preceding practical example is used, using a hydrogen-oxygen mixture or an acetylene-oxygen mixture as the combustion gas. The liquid is a reactive liquid such as TMOS (tetramethoxysilane). The droplets sprayed into the flame by electroflame spraying react there, e.g., when using TMOS, to form silica glass, and they are deposited on the substrate, this silica glass substrate being positioned a distance of 20 mm from the burner nozzle when using TMOS and a silica glass layer being sinter-fused directly on the substrate. In the same way, layers of other compositions can also be produced by using the corresponding liquids.

Citations

[12] Rosenbaum, S. and Clasen, R.: Preparing extremely finely dispersed free-flowing glass powders by means of electrospraying. In 71st Glass Technical Convention, 1977, Bayreuth.

[1] Venkatachari, K.R., et al., A combustion synthesis process for synthesizing nanocrystalline zirconia powders. J. Mater. Res., 1995. 10(3). p. 748–755.
[2] Katz, J.L. and P.F. Miquel, Syntheses and application of oxides and mixed oxides produced by a flame process. Nanostructured Materials, 1994. 4(5), p. 551–557
[3] Hung. C.-H. and J.L. Katz, Formation of mixed oxide powders in flames: Part I. TiO2-SiO2. J. Mater. Res., 1992. 7(7), p. 1861–1869.
[4] Karthikeyan, J., et al., Nanomaterial powders and deposits prepared by flame spray processing of liquid precursors. Nanostuctured Materials, 1997. 8(1), p. 61–74.
[5] Tikkanen, J., et al. Characteristics of the liquid flame spray process. Surface & Coatings Technology, 1997, 90, p. 210–216.
[6] Michelson, D., Electrostatic Atomization. ed. A. Hilger. 1990, New York.
[7] Chen, G. and Gomez, A., Burning of a quasi-monodisperse heptane electrospray in a counterflow diffusion flame. Chemical and physical processes in combustion, 1991, 109, p. 1–4.
[8] Chen G. and Gomez, A., Group combustion in co-flow laminar spray diffusion flames. Chemical and Physical Processes in combustion, 1995, p. 309–312.
[9] Zake, M., The excitation of gas particles in a flame in external electric field. Latvian J. Phys. & Techn. Sciences, 1995. (1), p. 10–18.
[10] Zake, M., The electric field effect on the interrelated heat and mass transfer in the flame. Latvian J. Phys. & Techn. Sciences, 1995. (3). p. 14–22.
[11] Nguyen, H.D. and Chung, J.N., Evaporation from a translating drop in an electric field. Int. Heat Mass Transfer, 1993. 36(15): p. 3797–3812.
[12] Rosenbaum, S. and Clasen, R., Herstellung von feinstteiligen rieselfähigen Glaspulvern durch Elektrosprühen. in 71. Glastechnische Tagung. 1997. Bayreuth

Claims

1. A method for producing aerosols, powders and layers made of glass and ceramics by means of electroflame spraying, **characterized by the fact that** with the help of an electric field between at least one flame and the surface of a liquid, at least one Taylor cone is created with the subsequent formation of an aerosol, yielding particles even down to the nanometer range.

2. The method according to Claim 1, characterized by the fact that the liquid is a melt of a material.

3. The method according to Claim 1, characterized by the fact that the liquid is a suspension of powder particles with particle diameters of 100 μm to 5 nm, predominantly 5 μm to 20 nm.

4. The method according to Claim 3, characterized by the fact that the dispersing liquid is evaporated at the latest before capturing the dispersed particles.

5. The method according to Claim 1, characterized by the fact that the liquid is a reactive liquid and particles are formed as a result of chemical reactions.

6. The method according to at least one of the Claims 1 through 5, characterized by the fact that the liquid is passed through at least one capillary and the liquid droplet at the end of the capillary is used as a liquid surface.

7. The method according to at least one of the Claims 1 through 5, characterized by the fact that the liquid rises due to capillary forces on a rod which is wetted by the liquid and which protrudes out of the surface of the liquid, with one or more Taylor cones developing at the tip.

8. The method according to at least one of the Claims 1 through 7, characterized by the fact that the particles in the flame are dispersed into numerous smaller, predominantly spherical particles.

9. The method according to at least one of the Claims 1 through 8, characterized by the fact that the particles are captured on a substrate and form a layer.

10. The method according to Claim 9, characterized by the fact that a uniformly thick layer is formed as a result of movement between the substrate and the spray flame.

11. The method according to Claims 9 and 10, characterized by the fact that the substrate reaches a temperature due to the flame or an additional heating such that the deposited particles can sinter or melt and form an adherent layer.

12. The method according to at least one of the Claims 1 through 11, characterized by the fact that the Taylor cone is formed at the center of several flames.

13. The method according to at least one of the Claims 1 through 11, characterized by the fact that several liquids are atomized [or: sprayed – translator] at the same time and multicomponent powders or multicomponent layers are formed due to chemical reactions or physical mixtures of the different liquids.

2 Pages of Drawing Appended

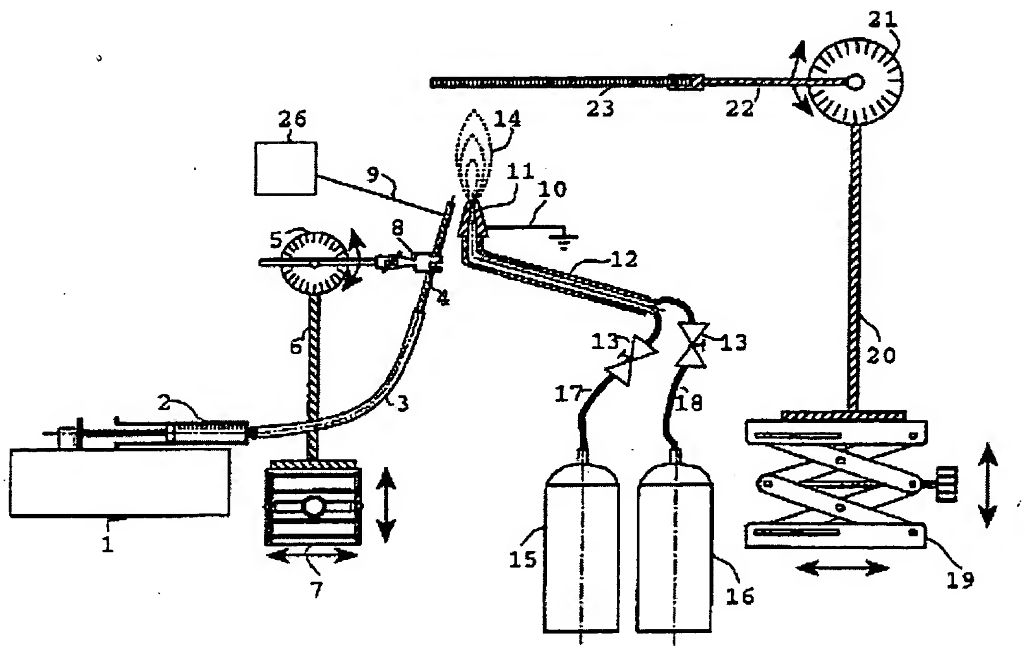

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Fig. 1

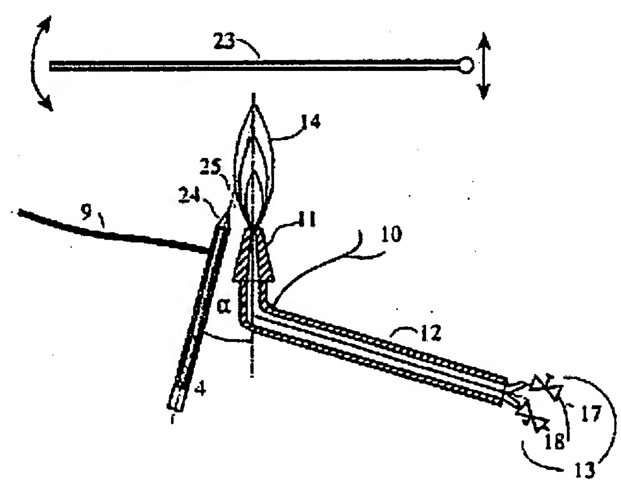
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Fig. 2

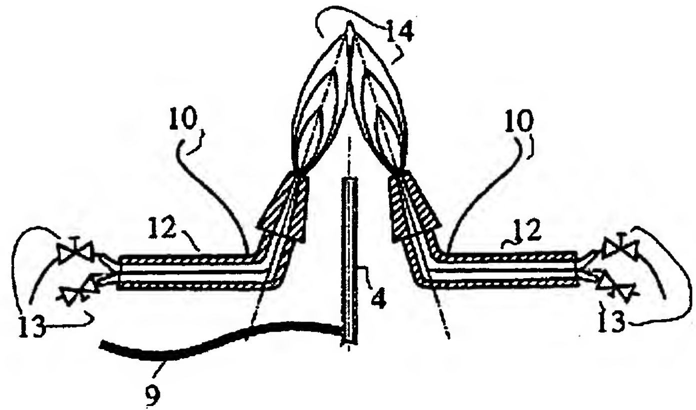

Fig. 3a

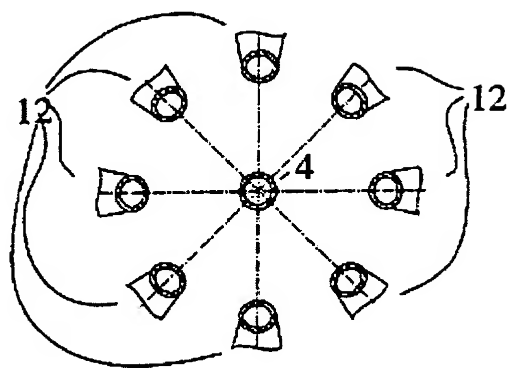

Fig. 3b